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Enhancing and modulating the intrinsic acidity of imidazole and pyrazole through beryllium bonds

Otilia Mó · Manuel Yáñez · Ibon Alkorta · José Elguero

Abstract The structure and electronic properties of the complexes formed by the interaction of imidazole and pyrazole with different $BeXH(BeX_2)$ (X = H, Me, F, Cl) derivatives have been investigated via B3LYP/6−311+G(3df,2p)//B3LYP/6−31+G(d,p) calculations. The formation of these azole:BeXH (BeX_2) complexes is accompanied by a dramatic enhancement of the intrinsic acidity of the azole, as the deprotonated azole is much more stable after the aforementioned interaction. Most importantly, the increase in acidity is so large that the azole:BeXH or azole:BeX_2 complexes behave as NH acids, which are stronger than typical oxyacids such as phosphoric acid and oxalic acid. Interestingly, the increase in acidity can be tuned through appropriate selection of the substituents attached to the Be atom, permitting us to modulate the electron-accepting ability of the BeXH or BeX_2 molecule.

Keywords Intrinsic acidity · Imidazole · Pyrazole · Beryllium bonds · DFT calculations

Introduction

The possibility of generating superbases [1–19] and superacids [20–35] in the gas phase has attracted a great deal of attention for many years. This interest is mainly due to the possibility of forming ion pairs in the gas phase [36–39] through spontaneous proton transfer from a superacid to a superbase. Most of the research performed in this area has focused on combining intrinsically strong acids with particular substituents in order to enhance their acidity. Another way of enhancing the intrinsic acidity of a system is by encouraging it to interact with a strong Lewis acid. This was first shown by Squires et al. for the specific case of BF_3–carbonyl complexes [40]. More recently, both experimental and theoretical work demonstrated that interacting different bases such as phosphines [41] and amines [42] with borane dramatically enhances the acidity of these compounds (upon comparing the ionization equilibrium constants, the acidity is enhanced by sixteen or seventeen orders of magnitude) [41]. It has also recently been predicted on theoretical grounds that the acidity of phosphines could be enhanced to an even degree if aluminum trihydride were to be used rather than borane [43]. However, although the hydrides of group III (BH_3, AlH_3, and GaH_3) and their derivatives are very good Lewis acids because they are intrinsically electron-deficient systems, beryllium derivatives also show significant Lewis acidity, and it was recently shown that they undergo very strong closed-shell interactions (termed "beryllium bonds") with typical Lewis bases [44]. Importantly, it was shown that beryllium bonds very strongly influence inter- or intramolecular hydrogen bonds, and vice versa [45]. In fact, the cooperativity between these two types of closed-shell interaction reinforces both of them [45]. The strengthening of both inter- and intramolecular hydrogen bonds when the hydrogen-bond donor forms beryllium bonds with a BeX_2 derivative appears to be a direct consequence of the increased acidity of the hydrogen-bond donor, which in turn is caused by the transfer of charge from this hydrogen-bond donor to the beryllium derivative. Therefore, we performed studies—as reported in this paper

O. Mó · M. Yáñez (✉)
Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, Campus de Excelencia UAM-CSIC, Cantoblanco, 28049 Madrid, Spain
e-mail: manuel.yanez@uam.es

I. Alkorta · J. Elguero
Instituto de Química Médica (IQM-CSIC), Juan de la Cierva, 3, 28006 Madrid, Spain

—that aimed to demonstrate that this is indeed the case, using the molecules of imidazole and pyrazole as benchmark cases. Our objectives were not only to prove that the acidities of these compounds increase significantly when they interact with BeX_2 derivatives, but also to show that this increase in acidity can be modulated through appropriate selection of the two X substituents. To achieve this, we considered the substituents X=H, CH_3, F, Cl.

Computational details

The theoretical model adopted in this study was the same one used in the first paper to report beryllium bonds as a new and characteristic type of closed-shell interaction [44]. This model is based on the use of B3LYP/6−31+G(d,p) optimized geometries and on final energies obtained using the same functional but a 6−311+G(3df,2p) basis set expansion. The harmonic vibrational frequencies and the thermal corrections to the entropy and the free energy were evaluated at the same level used for the geometry optimizations. This model, which has proven to be very reliable for describing beryllium bonds using CCSD(T) high-level ab initio calculations as a reference [44], has also been found to be very reliable for calculating intrinsic acidities [46].

One important aspect of the rationalization of the increase in the acidity of the azoles investigated here when they form complexes with BeX_2 derivatives is the alterations in bonding perturbation associated with charge transfer from the azole, which acts as a Lewis base to the BeX_2 moiety (the Lewis acid) [44]. A very efficient way of characterizing the charge transfers is through NBO second-order perturbation analysis [47] of the occupied orbitals of the base and the empty orbitals of the acid, so this was one of the approaches used in the present work. Simultaneously, it is also possible to estimate the populations of the initially empty orbitals of the Lewis acid as an alternative measurement of the degree of charge transfer. The calculation of the Wiberg bond order [48] within the same framework provides a reliable measure of the changes in the strengths of the bonds in both interacting moieties.

A complementary view of the perturbations to the bonding in both the Lewis base and the Lewis acid can be achieved through the use of the atoms in molecules (AIM) theory [49, 50]. For this purpose, we obtained the molecular graphs defined by the ensemble of local maxima of the electron density, saddle points (usually named "bond critical points"), and the lines of zero density gradient connecting them (usually named "bond paths"). We paid particular attention to changes in the electron density at the bond critical points (BCPs), because these changes are a clear indication

of bond reinforcements (if the density increases) or bond weakening (if the density decreases). The value of the energy density at the BCP is a good index of the nature of the interaction.

Results and discussion

The optimized structures of the complexes formed by imidazol and pyrazole with BX_2 and BeXH (X = H, CH_3, F, Cl) are summarized in Table S1 of the "Electronic supplementary material" (ESM). The calculated intrinsic acidities (in terms of both enthalpy and free energy) are summarized in Table 1.

When the Lewis acid is a BeHX (X = F, Cl) derivative, there are two possible conformers depending on the relative orientation of the BeHX moiety with respect to the azole molecule (see Scheme 1). For neutral pyrazole and imidazole complexes, tautomer (a) is slightly more stable than tautomer (b). Conversely, for the deprotonated species, tautomer (b) is slightly more stable than tautomer (a). These differences in stability are smaller than 1 $kJmol^{-1}$ for the imidazole complexes, so the effect on the calculated acidity is never larger than 1.5 $kJmol^{-1}$. The differences are more significant (around 5 $kJmol^{-1}$) when pyrazole complexes are considered, so the difference in acidity between complexes (a) and (b) can be as large as 9 $kJmol^{-1}$. This is likely due to the fact that for pyrazole, the stability of the neutral complex is enhanced due to a favorable interaction between X (= F, Cl) and the hydrogen of the NH group, whereas the stability of the deprotonated form should be slightly less favorable because the proton was removed. For the sake of simplicity, we have included only the acidity of the most acidic tautomer in Table 1.

From the values reported in Table 1, it is apparent that the complexation of imidazole and pyrazole with BeHX and BeX_2 derivatives produces a huge increase in the intrinsic acidity of the azole. It is worth noting the very good agreement between our theoretical estimates for the two isolated parent compounds and the most recent experimental values. This clearly indicates that we can be confident in the accuracy of our predictions regarding the acidity of the complexes under scrutiny here. To get a more realistic idea of what this acidity enhancement implies, it is important to realize that all the complexes included in this survey are predicted to be stronger acids than phosphoric acid, whose experimental gas-phase acidity is ΔH_{acid}=1383. ± 21. (ΔG_{acid}=1351. ± 21) $kJmol^{-1}$ [53]. Note also that both Im:$BeCl_2$ and Pyr:$BeCl_2$ complexes are stronger acids than oxalic acid (ΔH_{acid}=1356. ± 8.4; ΔG_{acid}=1323. ± 8.4 $kJmol^{-1}$) [54]. This means that the complexation of

Table 1 Intrinsic acidities (ΔH_{acid} and ΔG_{acid}, in kJmol^{-1}) of imidazole, pyrazole, and their BeXH and BeX$_2$ (X = Me, F, Cl) complexes, and the increases in the acidity [$\Delta(\Delta H_{acid})$ and $\Delta(\Delta G_{acid})$], in kJmol^{-1} of these complexes with respect to the acidities of their isolated parent compounds

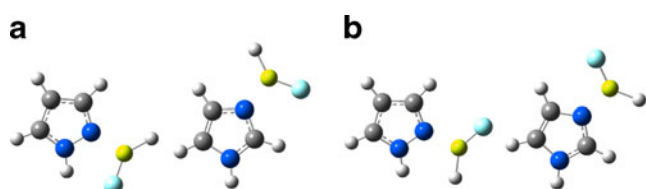| System	ΔH_{acid}	ΔG_{acid}	$(\Delta(\Delta H_{acid}))$	$(\Delta(\Delta G_{acid}))$	ΔH_3^0 [ΔG_3^0]	ΔH_4^0 [ΔG_4^0]
Imidazole (Im)	1467.1[a]	1435.6[a]	0	0		
Im:BeH$_2$	1354.7	1323.7	112.4	111.9	−114.4	−226.8
					[−74.3]	[−186.2]
Im:BeMe$_2$	1357.6	1320.7	109.4	114. 9	−73.8	−183.2
					[−22.6]	[−141.1]
Im:BeFH	1352.9	1321.8	114. 2	113.8	−109.9	−224.1
					[−67.5]	[−181.3]
Im:BeF$_2$	1349.2	1318.0	117.9	117.6	−122.9	−240.8
					[−92.5]	[−210.1]
Im:BeClH	1336.9	1305.3	130.2	130.3	−122.6	−252.8
					[−78.4]	[−208.7]
Im:BeCl$_2$	1323.6	1291.7	143.5	143.9	−139.3	−282.8
					[−96.6]	[−240.5]
Pyrazole(Pyr)	1487.2[b]	1455.4[b]	0	0		
Pyr:BeH$_2$	1378.9	1347. 2	108.3	108.2	−113.6	−221.9
					[−73.0]	[−181.2]
Pyr:BeMe$_2$	1377.2	1346.6	110.0	108.8	−71.5	−181.6
					[−26.6]	[−135.4]
Pyr:BeFH	1371.6	1340.3	115.6	115.1	−106.1	−221.7
					[−63.2]	[−178.3]
Pyr:BeF$_2$	1370.4	1337.8	116. 8	117.6	−119.7	−236.5
					[−88.2]	[−205.8[
Pyr:BeClH	1354.8	1322.9	132.4	132.5	−116.6	−249.0
					[−74.5]	[−207.0]
Pyr:BeCl$_2$	1344.3	1311.1	142.8	144.3	−135.1	−277.9
					[−91.8]	[−236.1]

[a] Experimental gas-phase acidity: $\Delta H_{acid}=1464.1\pm3.0$ and $\Delta G_{acid}=1433.4\pm1.7$ kJmol^{-1} (taken from [51])

[b]Experimental gas-phase acidity: $\Delta H_{acid}=1479.\pm10.$ and $\Delta G_{acid}=1449.\pm9.6$ kJmol^{-1} (taken from [52])

imidazole and pyrazole with BeHX and BeX$_2$ derivatives not only enhances their acidity but changes these two typical imino bases into N–H acids, which are stronger than some oxyacids.

The origin of this acidity enhancement is similar to that reported for phosphine boranes [41], phosphine alanes [43], and aminoboranes [42]. As we shall discuss later, the large charge transfer typically involved in the formation of a beryllium bond renders the azole more electron deficient, leading to a significant increase in the intrinsic acidity of its NH group. Although this effect causes a rather moderate increase in the natural charge of its H atom, which goes from +0.45 in the isolated azole to +0.47 in the complexes with BeCl$_2$, this

change is strongly reflected in the value of the molecular electrostatic potential, which increases by 92 and 31 kJmol^{-1} for imidazole and pyrazole, respectively, upon BeCl$_2$ association. It is worth noting that the effect is smaller for pyrazole than for imidazole, reflecting the favorable interaction (as mentioned above) between the acidic NH group and the BeCl$_2$ molecule for the particular case of pyrazole. However, a much more precise and quantitative model for rationalizing the calculated increase in acidity is provided by the thermodynamic cycle shown in Scheme 2.

Scheme 1 Possible conformers of the complexes formed by the interaction of pyrazole and imidazole with BeHX (X = F, Cl) derivatives
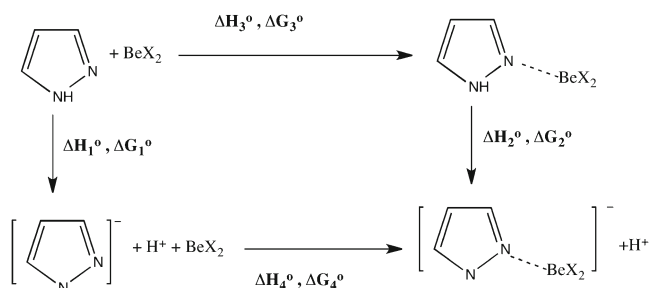
Scheme 2 Thermodynamic cycle relating the intrinsic acidity of pyrazole and pyrazole-BeX2 complexes with the stabilization of neutral and deprotonated pyrazole by association with BeX2 derivatives

In this cycle, using pyrazole as a suitable model system, the intrinsic acidity of the isolated azole is measured by ΔH_1^0 (ΔG_1^0), whereas ΔH_2^0 (ΔG_2^0) measures the intrinsic acidity of the pyrazole:BeX_2 complex. Accordingly, ΔH_3^0 (ΔG_3^0) and ΔH_4^0 (ΔG_4^0) measure the stabilization of the neutral and the deprotonated pyrazole, respectively, when they interact with BeX_2. The calculated increase in acidity associated with the formation of the Pyr:BeX_2 complex necessarily implies that ΔH_4^0 (ΔG_4^0) are significantly larger than ΔH_3^0 (ΔG_3^0); i.e., that BeX_2 stabilizes the deprotonated pyrazole much more than the neutral pyrazole. Indeed, as shown in Table 1, ΔH_4^0 varies between 180 and 280 kJmol^{-1}, whereas ΔH_3^0 varies between 74 and 140 kJmol^{-1}. It is worth noting that the stabilization produced by the beryllium bonds is about 40–50 kJmol^{-1} smaller in terms of free energy, because complex formation is accompanied by a decrease in entropy of approximately 130 Jmol^{-1}K^{-1} on average. However, this decrease is very similar for both the neutral and the deprotonated complexes, so the increase in acidity is practically the same whether measured in terms of enthalpy or free energy.

The greater stabilization of the deprotonated azoles actually reflects their enhanced electron-donation capacities with respect to their neutral counterparts. Indeed, deprotonation leads to an electron rich system with a HOMO that is much higher in energy than the HOMO of the neutral species it derives from. This, together with the fact that the beryllium derivatives are electron-deficient systems, results in rather large [azole–H]$^-$–
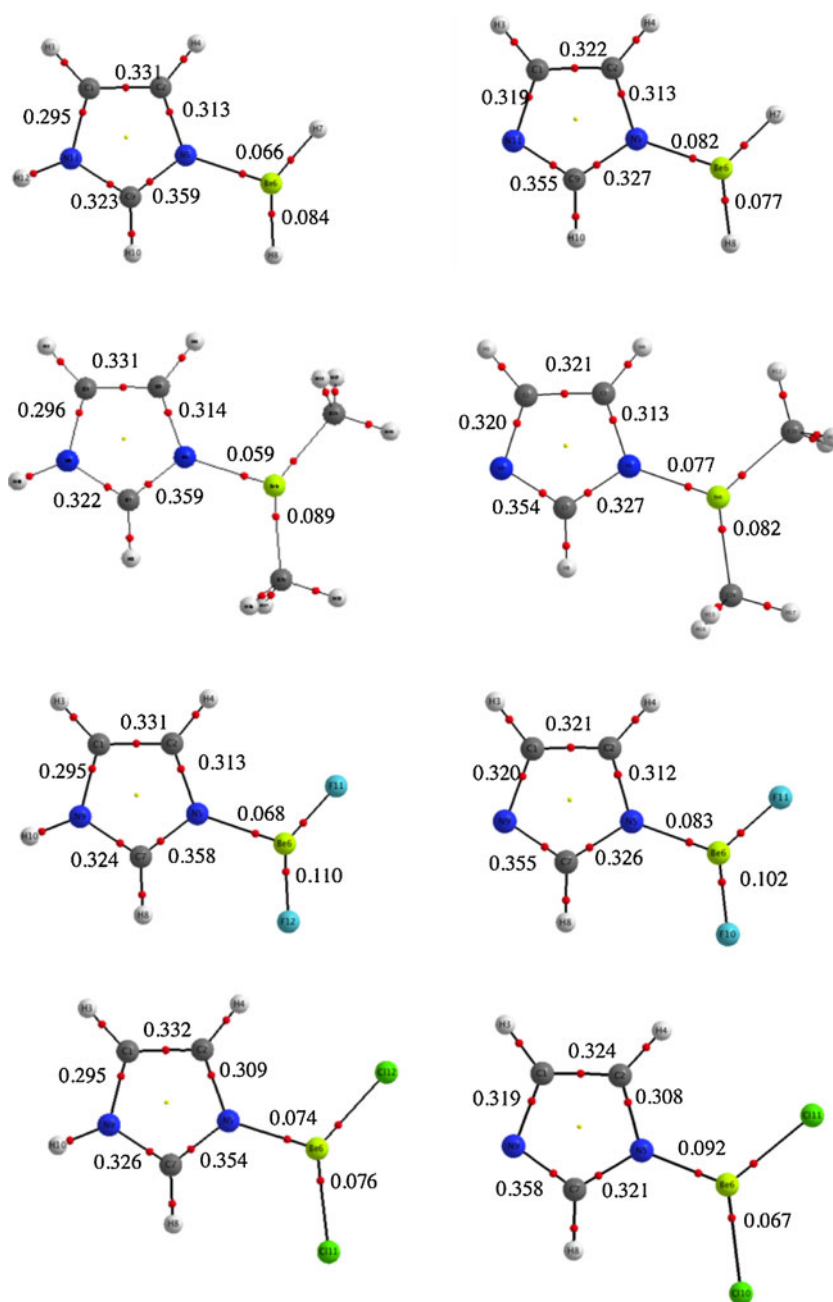
BeX_2 (BeXH) interaction energies. In fact, as illustrated in Table 2 for all the complexes involving neutral azoles, there is a strong interaction between the lone pair of the imino nitrogen in the azole and the empty p orbital of the Be atom. This donation is actually responsible for the bending of the BeXH or BeX_2 moiety. Also, charge transfer occurs towards the σ_{BeX}* antibonding orbital at the same time, and this is responsible for the elongation of the Be–X bonds on going from the isolated BeXH or BeX_2 Lewis acid to the azole:BeXH (BeX_2) complex (see Table S1 of the ESM). In principle, the mechanism is the same when the complex involves the deprotonated azoles, but the much stronger interaction between the N lone pair and the Be orbitals means that the NBO analysis identifies it as a new, very polar N–Be covalent bond that is dominated by the contribution (about 90 %) from the hybrid orbitals on N (see Table S2 of the ESM), except in the case of the BeF_2 complex. It is also worth noting that the Wiberg bond index systematically increases with complex deprotonation.

This description is also in accord with that obtained using the AIM theory. As shown in Fig. 1, for imidazole complexes, there is a significant increase in the electron density at the N–Be bond critical point upon going from neutral to deprotonated complexes, whereas the electron density at the Be–X bond critical points simultaneously decreases. The same behavior is exhibited by pyrazole complexes, as shown in Figure S1 of the ESM.

Table 2 Characteristics of the N–Be interaction in neutral complexes of imidazole and pyrazole with BeXH and BeX_2 (X = H, Me, F, Cl) derivatives in terms of the second-order orbital interaction energies (in kJmol^{-1}) or in terms of the N and Be hybrid orbitals that participate in the N–Be covalent bond. The Wiberg bond indices (WBIs) for neutral and deprotonated forms are also given

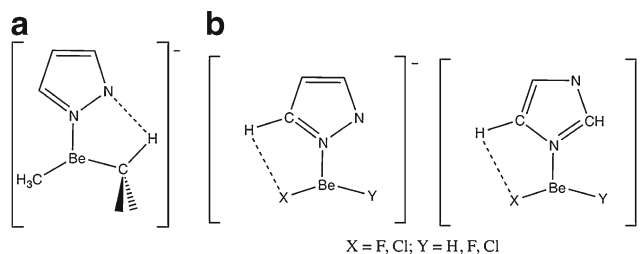| System	N–Be bonding	WBI	
	Neutral	Neutral	Deprotonated
Im:BeH$_2$	LP(N) → Be(2p) 431 LP(N) → σ_{BeX}* 20	0.327	0.418
Im:BeMe$_2$	LP(N) → Be(2p) 383 LP(N) → σ_{BeX}* 24	0.299	0.384
Im:BeFH	LP(N) → Be(2p) 436 LP(N) → σ_{BeX}* 12	0.303	0.384
Im:BeF$_2$	LP(N) → Be(2p) 467 LP(N) → σ_{BeX}* 18	0.287	0.363
Im:BeClH	91%N(39 %s + 61 % p) +9%Be(26 %s + 73%p)	0.335	0.548
Im:BeCl$_2$	LP(N) → Be(2p) 483 LP(N) → σ_{BeX}* 14	0.335	0.413
Pyr:BeH$_2$	LP(N) → Be(2p) 458 LP(N) → σ_{BeX}* 32	0.345	0.419
Pyr:BeMe$_2$	LP(N) → Be(2p) 407 LP(N) → σ_{BeX}* 33	0.315	0.496
Pyr:BeFH	LP(N) → Be(2p) 460 LP(N) → σ_{BeX}* 43	0.321	0.387
Pyr:BeF$_2$	92%N(40 %s + 60 % p) +8%Be(30%s +70%p)	0.299	0.370
Pyr:BeClH	LP(N) → Be(2p) 490 LP(N) → σ_{BeX}* 38	0.356	0.419
Pyr:BeCl$_2$	LP(N) → Be(2p) 508 LP(N) → σ_{BeX}* 20	0.353	0.541

Fig. 1 Molecular graphs for the complexes of imidazole or its deprotonated form with BeX$_2$ (X=H, Me, F, Cl) derivatives. *Red and yellow dots* denote BCPs and ring critical points, respectively. Electron densities are in a.u.

Although in all cases the acidity enhancement is huge, the values in Table 3 show that this enhancement is slightly larger, in relative terms, for pyrazole than for imidazole.

Table 3 Relative acidity enhancement ($\Delta(\Delta H_{acid})$, kJmol^{-1}) as a function of the nature of the beryllium derivative that interacts with the azole. BeH$_2$ was used as the reference in all cases

Be derivative	Imidazole $\Delta(\Delta H_{acid})$	Pyrazole $\Delta(\Delta H_{acid})$
BeH$_2$	0.0	0.0
BeMe$_2$	−3.0	+1.8
BeFH	+1.8	+7.3
BeF$_2$	+5.5	+8.5
BeClH	+17.8	+24.1
BeCl$_2$	+31.1	+34.5

X = F, Cl; Y = H, F, Cl

Scheme 3 Intramolecular non-covalent interactions responsible of the enhanced stability of complexes between deprotonated pyrazole and BeXY derivatives

In fact, whereas Im:BeMe$_2$ is predicted to be 3 kJmol^{-1} less acidic than Im:BeH$_2$, the pyrazole analog Pyr:BeMe$_2$ is predicted to be 1.8 kJmol^{-1} more acidic than Pyr:BeH$_2$. This difference can be accounted for by the noncovalent interaction between the H atom of the methyl group in the deprotonated Pyr:BeMe$_2$ complex [see structure (a) in Scheme 3] and the deprotonated N atom, which helps to stabilize the anion but is not possible in the imidazole analog.

For the remaining complexes involving BeXH or BeX$_2$ (X=F, Cl) derivatives, the slightly larger relative acidity enhancement of pyrazole complexes is likely related to weak noncovalent interactions, such as that between the halogen atom of the BeXH(BeX$_2$) moiety and the CH group attached to the imino nitrogen of the azole (see structures (b) in Scheme 3). In fact, inspection of the natural charges shows that the charge on the H atom of the CH group that interacts with the halogen is slightly larger (+0.24 e) in pyrazole than in imidazole complexes (+0.22 e), whereas the net charge of the halogen atom X is slightly more negative. This slightly stronger interaction in pyrazole complexes is actually reflected in a shorter (~0.2 Å) X$\cdots$H distance. It can also be observed that the acidity enhancement is larger for BeHCl and BeCl$_2$ complexes than for their corresponding F-containing analogs. This is due to the different effects of the Lewis acid deformation on the interaction energies, as has been explained for similar complexes involving ammonia as a Lewis base [55].

Importantly, as is evident from Table 3, this enhancement can be tuned by appropriate selection of the substituents attached to the Be atom, because the electron-accepting ability of the BeXH(BeX$_2$) moiety is dependent on the electronegativity of the substituent attached to the metal.

Conclusions

The association of imidazole and pyrazole with different BeXH(BeX$_2$) derivatives leads to dramatic increases in the intrinsic acidities of these azoles. The formation of the beryllium bond implies significant charge transfer from the lone pair on the imino nitrogen into the empty p orbital of Be, and the charge transfer is significantly larger for the deprotonated than for the neutral azole. This results in greater stabilization of the deprotonated anion and thus a huge increase in the acidity of the azole. Most importantly, the acidity enhancement is so large that azole:BeXH or azole:BeX$_2$ complexes behave as NH acids, which are stronger than typical oxyacids such as phosphoric or oxalic acid.

The increase in the acidity is very similar for both imidazole and pyrazole complexes, although it is slightly larger for the pyrazole than for the imidazole complexes due to the role played by noncovalent interactions in the anion. The acidity

enhancement can be tuned by appropriate selection of the substituents attached to the Be atom, which can modulate the electron-accepting ability of the BeXH or BeX$_2$ molecule.

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